

ON DETERMINING IMPORTANT ASPECTS OF MATHEMATICAL MODELS:

APPLICATION TO PROBLEMS IN PHYSICS AND CHEMISTRY*

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SUMMARY

Mathematical modelling must always deal with two general problems. First, the form, parameters or distributed functions in a mathematical model are often imprecisely known and their impact on desired objectives or observables is an important issue. Second, even when the components in a model are "known" there always remains the fundamental question concerning the importance and interrelationship between the various components of the system. The use of parametric and functional gradient sensitivity analysis techniques is considered for models described by partial differential equations. By interchanging appropriate dependent and independent variables, questions of inverse sensitivity may be addressed to gain insight into the inversion of observational data for parameter and function identification in mathematical models. It may be argued that the presence of a subset of dominantly strong coupled dependent variables will result in the overall system sensitivity behavior collapsing into a simple set of scaling and self similarity relations amongst elements of the entire matrix of sensitivity coefficients. These general tools are generic in nature, but the present paper will emphasize their application to problems arising in selected areas of physics and chemistry.

INTRODUCTION

Mathematical modelling and analysis has been a traditionally active area in engineering and this is especially true in recent years with the ready availability of high-speed digital computers. Such modelling efforts have many goals, including design, optimization and merely understanding the systems' components. As an adjunct to these efforts, the tools of sensitivity analysis provide a natural means to aid in all of these goals and the development of the subject in engineering has been especially focused on applications to design and optimization. The ultimate driving force behind all these efforts is certainly the practical issues of increased reliability, efficiency, etc.

An interesting contrast with the modelling/sensitivity analysis efforts primarily in engineering occurs upon consideration of analogous problems in the "fundamental" areas of chemistry and physics. The first point of contrast is that issues of design and optimization are frequently not relevant in basic

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research studies of chemistry and physics (studies involving problems in applied physics, industrial chemical processes, etc. would be best categorized as engineering). The term "modelling" is also rarely used in the scientific disciplines and the basic thrust is usually for an attainment of system understanding. In particular, control variables frequently found in engineering problems are often absent in the physical and chemical events occurring at atomic and molecular scales. The lack of practical motivation and these inherent differences between engineering and scientific problems has apparently resulted in only a recent realization that the tools of sensitivity analysis have a potentially valuable contribution to make in chemistry and physics.¹⁻⁶

The differences cited above obscure the overall basic similarity between mathematically defined engineering and scientific problems. Their common foundation lies in their basic input-output nature. In addition, the particular mathematical formulations involved can be quite similar even though the physical interpretation is different (e.g., the equations of stationary quantum mechanics are exactly those of classical linear waves). From this general perspective, a common set of tools may be developed within the framework of sensitivity analysis of benefit to all the relevant disciplines making use of mathematical modelling techniques. The present paper will succinctly review current activity with the topics being primarily in the area of chemical physics. Special emphasis will be given viewing problems from a functional perspective rather than treating them as described by a discrete set of input parameters. This approach is essential in many scientific applications and often has a similar broad basis in engineering. Although the particular applications discussed in the paper require more information than provided here for a full appreciation of their significance, they should be viewed in a generic context for analogous applications in other possible areas of interest to the reader. Finally, due to the brief nature of this paper, no attempt will be made to thoroughly review all recent developments in sensitivity analysis as applied to chemical physics problems; a series of recent review articles is available to cover this literature.¹⁻⁶

BASIC CONCEPTS OF FUNCTIONAL SENSITIVITY ANALYSIS

The problems of interest in chemical physics at the atomic scale or macro scale are typically described by differential equations of a boundary value and/or initial value nature. For example, Schrödinger's equation in quantum mechanics has the form

$$\left[\frac{\hbar}{i} \frac{\partial}{\partial t} - \frac{\hbar^2}{2m} \nabla^2 + V(\underline{r}) \right] \psi = 0$$

and the equations of mass conservation in chemical kinetics have the form

$$\frac{\partial}{\partial t} C_i - D_i \nabla^2 C_i - f_i(C) = 0$$

These latter equations follow conventional notation where \hbar is Planck's constant, m is the mass of the particle interacting with potential $V(\underline{r})$ and its wavefunction $\psi(\underline{r}, t)$ is evaluated at point \underline{r} and time t , while C_i is the i -th

chemical species concentration, D_i is the corresponding diffusion coefficient and the reactive flux f_i is generally a nonlinear function of the concentrations. Although Schrödinger's equation is rigorously the only valid approach for treating dynamics at the atomic scale, classical mechanics is a very popular and often quite accurate approach to treating the motion of atoms and molecules. In this case, Hamilton's equations

$$\frac{\partial q_i}{\partial t} = \frac{\partial H}{\partial p_i}, \quad \frac{\partial p_i}{\partial t} = - \frac{\partial H}{\partial q_i}$$

would apply where $H(p,q)$ is the Hamiltonian with i -th coordinate q_i and momentum p_i . Various other dynamical equations also occur in statistical mechanics and in models occurring in all aspects of chemical physics. A general situation commonly arising, included in the equations above, is the appearance of coefficients which are functions of either the system independent or dependent variables. For example, the potential $V(\underline{r})$ plays this role in Schrödinger's equation. These functions may be thought of as input, and two broad categories will arise. First, the form of these functions may be imprecisely known due to a lack of full understanding of the system or simply imprecise measurements defining the structure of the functions. Second, even if the input functions are known precisely, there is typically a very poor understanding of how the form or structure of these functions influences the behavior of the equation solutions or observables. As mentioned in the Introduction, the possibility of varying these functions for the purpose of optimization will not be explicitly considered here since this is not often the case. Therefore, the role of sensitivity analysis in chemistry and physics is largely to provide a means to probe the interrelationship between the input and output functions (i.e., determine the important aspects of the system).

In order to better quantify the above discussion, we may generally write any of the appropriate differential equations in the following form

$$L_i(\underline{r}, t, \underline{\theta}) = 0 \quad (1)$$

where L_i is the i -th differential operator typically being a nonlinear function of the elements of the output solution vector $\underline{\theta}(\underline{r}, t)$. Appropriate initial and/or boundary conditions would be given in order to completely specify the problem. The parametric functional nature of the differential equations is evident through the arguments of L_i in Eq. (1) depending on position \underline{r} and time t . In addition, the boundary conditions may be functions of time and the initial conditions may be functions of position also acting as another class of input functions for consideration. Regardless of the circumstance, we may generally denote the vector of input functions as $\underline{\Omega}(\underline{r}, t)$ and the first variation of Eq. (1) becomes

$$\sum_n \frac{\partial L_i}{\partial \theta_n} \frac{\delta \theta_n(\underline{r}, t)}{\delta \theta_l(\underline{r}', t')} + \frac{\delta L_i}{\delta \Omega_l} = 0 \quad (2)$$

The first of these terms in Eq. (2) involves the system Jacobian $\partial L_i / \partial \theta_n$, and the second term is the explicit functional derivative of the operator with

respect to the l -th member of the input function set. The solution to this linear differential equation produces the functional derivative matrix $\delta\phi_n(\underline{r},t)/\delta\Omega_l(\underline{r}',t')$ giving the response of the n -th output at position \underline{r} and time t with respect to a disturbance of the l -th input function at position \underline{r}' and time t' such that

$$\delta\phi_n(\underline{r},t) = \sum_l \int d\underline{r}' dt' \frac{\delta\phi_n(\underline{r},t)}{\delta\Omega_l(\underline{r}',t')} \delta\Omega_l(\underline{r}',t') \quad (3)$$

where $\delta\Omega_l(\underline{r}',t')$ is an arbitrary infinitesimal functional variation. The matrix solution to Eq. (2) constitutes what is sometimes referred to as the forward sensitivity matrix. All of the general applications of sensitivity analysis in chemical physics have focused on an examination of the sensitivity matrix elements and perhaps most importantly their manipulation to address other questions besides mere input-output relations. This point will be emphasized later in this paper.

Since Eq. (2) is linear, it is quite natural to define a Green's function matrix with elements $\delta\phi_n(\underline{r},t)/\delta g_l(\underline{r}',t')$ having the general interpretation of the response of ϕ_n to a disturbance of the flux g_l of the l -th member of the dependent variable set. This matrix satisfies the following equation

$$\sum_n \frac{\partial L_i}{\partial \phi_n} \frac{\delta\phi_n(\underline{r},t)}{\delta g_l(\underline{r}',t')} = \delta_{il} \delta(\underline{r}-\underline{r}') \delta(t-t') \quad (4)$$

The solution to Eq. (2) may be directly expressed in terms of the Green's function solution to Eq. (4). In some cases, this can be a practical numerical procedure but more importantly the elements of the Green's function matrix have direct physical significance and in principle measurements in the laboratory could be performed to determine them. This latter point is especially important since as commented above many basic problems in chemistry and physics do not inherently contain laboratory control functions or variables.

Equation (2) produces the first order functional perturbation coefficients to the nominal solution of Eq. (1) as evidenced by Eq. (3). Due care is needed if the physics corresponds to a degenerative perturbation problem. Standard procedures exist in this case corresponding to the introduction of directional derivatives. A variety of numerical techniques have been developed for solving Eqs. (2) or (4), and detailed information may be found in the literature. In general, it seems most efficient to solve Eq. (2) by maximally taking advantage of its structure in relation to the often employed Newton linearization schemes applied to Eq. (1).

In practice, the coupled differential equations in Eq. (1) are often highly nonlinear and an interesting type of scaling behavior has been found under certain conditions.* This situation has not been explored for the case of functional variations, except for the Green's function, and for that reason we shall consider it here in terms of discrete system parameters denoted by the vector \underline{a} . Supposing that a single dominant dependent variable exists one might expect that a variation in any given system parameter would show up as significant, provided that the dominant variable significantly responded.

*H. Rabitz and M. Smooke, "Scaling Relations and Self Similarity Conditions in Strongly Coupled Dynamical Systems", J. Phys. Chem., in progress.

Without loss of generality, we may take the dominant dependent variable as $\phi_1(t, \underline{\alpha})$ where time t is taken as the only independent "coordinate" for simplicity. Often the identification of this dominant variable seems to be associated with the most strongly coupled nonlinear member entering the differential equations. Under the assumption of strong dominant dependence, we may approximate the remaining dependent variables as

$$\phi_n(t, \underline{\alpha}) \approx \mathcal{F}_n(\phi_1(t, \underline{\alpha})) \quad (5)$$

where \mathcal{F}_n is an appropriate function. The important point is that the parameter dependence of all the remaining dependent variables is approximately driven through that of the dominant dependent variable. This is in keeping with the notion that the dominant variable will pass judgment over any parameter variation regarding its significance to any of the remaining dependent variables. A natural consequence of the approximation in Eq. (5) is the scaling relation

$$\left[\frac{\partial \phi_n}{\partial \alpha_i} \right] \approx \left[\frac{\partial \phi_1}{\partial \alpha_i} \right] \left[\frac{\partial \phi_n}{\partial \phi_1} \right] \left[\frac{\partial \phi_1}{\partial t} \right]^{-1} \quad (6)$$

which expresses all the system sensitivities in terms of those of the dominant dependent variable and simple temporal slope information. The full significance of scaling behavior has not been established although it may have wide applicability in nonlinear systems outside of chemistry and physics.

A MENU OF SENSITIVITY APPLICATIONS IN CHEMICAL PHYSICS

It is beyond the scope and purpose of this paper to present detailed, elaborate physical analyses of particular models or problems. Rather, the examples should be viewed for their generic behavior and as illustrations of the type of sensitivity technology existing in chemical physics (specific citations to the literature can be found in refs. 1-6). The best means to present this information appears to be in the narrative tabular form given below. Finally, many of the examples carried out thus far in chemical physics have considered discrete parameter systems rather than those prescribed from a functional point of view. This approach was taken even though the physical problems were functional in nature. Although these studies were often insightful, a number of cases clearly indicate that the use of a small number of discrete parameters to represent typical continuous input functions can give misleading sensitivity results at times. This comment would most assuredly be applicable to situations outside the realm of chemical physics.

A. Forward Sensitivities

A direct analysis of the gradients introduced in Eq. (2) comprises the forward problem. The name forward results from the fact that the system is being analyzed from the forward direction whereby the response of the output to a disturbance of the input is examined. The magnitude, sign and general

behavior of the sensitivity coefficients as a function of their arguments is of concern. This comment applies to all of the other applications in the following paragraphs. A wealth of information can be gleaned by such an analysis and a number of applications have been carried forth. For example, in the case of molecular collisions, the role of different regions of the potential function upon the collision cross section has been explored. For elastic, inelastic and reactive scattering, a wide variety of problems have been treated in chemical kinetics encompassing temporal, steady-state spatial and unsteady spatial systems.

B. Inverse Sensitivities

The forward sensitivities in paragraph A correspond to the logical definition of the system parameters or input functions as independent variables and the system observables as dependent variables. The original physical problem is, of course, cast in this framework but many laboratory or field measurements are actually done for the purpose of inversion to better quantify a model. In this sense, one may use a "reasonable" zeroth order model and the accompanying forward sensitivities to calculate corresponding inverse sensitivities. These may be denoted as $\partial\Omega_l(\underline{r},t)/\partial\phi_n(\underline{r}',t')$ and it is evident that they give information on the infinitesimal response of the l -th function in the model to a disturbance of the n -th member of the observation set. Knowledge of these gradients can be used as a means to design possible experiments for the ultimate purpose of inversion. In principle, they may also be employed in an iterative inversion process with real data. Thus far, applications in chemical physics have been confined to the former case. Illustrations have been performed for inverse molecular scattering and chemical kinetics mechanism identification. These inverse sensitivities are the first members of what has been referred to as derived sensitivities since they may be derived from the forward set in paragraph A above. The forward and inverse sensitivities are orthogonal complements of each other and more generally they are related through Legendre type transformations familiar in thermodynamics. Exactly the same techniques are employed to generate the specialized sensitivities in paragraph C and D below.

C. Parameter Interrelationships

As implied in paragraph B, one may relax the constraints on the original definition of the system dependent and independent variables or some portion thereof. In this fashion, it is possible to calculate the possible response of one system input function to a disturbance of another corresponding to the gradients $\partial\Omega_l(\underline{r},t)/\partial\Omega_k(\underline{r}',t')$. Nonzero values for these parameter correlation gradients would imply a relationship between the input functions under the particular constraint relaxing the role of the system dependent and independent variables. The behavior of these gradients has implication for the uniqueness of the system model.

D. Observation Interrelationships

A family of gradients exactly analogous to those in paragraph C can be generated to study the relationship between different possible observations or dependent variables in a system. This is a physically meaningful question since all possible observations or system behaviors derive from the same underlying model. The particular gradients in this case have the form $\delta\theta_n(\underline{r},t)/\delta\theta_m(\underline{r}',t')$ where it is understood that an implied exchange of dependent and independent variables has occurred. As with the inverse gradients in paragraph B, these new sensitivities are also of use in the design of laboratory or field measurements. Nonzero values for these gradients imply a relationship between two possible observations and in that case serious consideration should be given to whether it is worthwhile to actually perform both measurements. A hierarchy of observations could be established based on the magnitude of these families of gradients. Little application has thus far been carried out along these lines.

E. Flux Disturbance Sensitivities

The Green's function introduced as the solution to Eq. (4) corresponds to the literal situation of disturbing one of the system dependent variables and monitoring a response in another. Knowledge of such responses provides a detailed map of the interconnectivity produced by the physical model. An interesting point in this regard concerns the fact that the dynamic response of the actual model can be quite distinct from that implied by the kinematic structure of the differential equations. A mapping of the system dependent variable interconnectivity can give valuable insight into which components or portions of a model are of actual significance to the questions or observations of concern. Green's functions are routinely calculated in a variety of applications in chemical physics for these reasons.

F. Objective Function Sensitivity Analysis

As discussed in the Introduction, many problems in chemical physics are not posed with well understood observational objectives before actually investigating the problem. Indeed, the general role of sensitivity analysis in chemical physics is often to simply identify interesting objectives or model components worth further study theoretically and experimentally. This perspective is typically at variance with the situation found in engineering where the problem is often first posed by stating the desired objective. In general, any observable feature or objective of the system may be written as a functional $F[\theta]$ of the system dependent variable vector. Direct functional differentiation of this object will probe the desired quantity of interest in a straightforward fashion. An interesting point occurs when this objective can be identified before actually solving the model. In this circumstance, the well know adjoint sensitivity analysis method may be employed to efficiently calculate the sensitivities of the system objectives. This latter procedure has only been used sparsely in chemical physics thus far for the evident reasons stated above.

G. Model Reduction

A natural objective in all modelling efforts is to reduce the system complexity to a level suitable for the questions or tasks at hand. A procedure such as this is sometimes referred to as lumping, and sensitivity coefficients provide information relevant to this goal. The forward sensitivity coefficients in paragraph A may be examined for this purpose and this is routinely performed. Related more sophisticated manipulation of these forward sensitivities can also be considered but much more work needs to be done in this area to optimally draw on the full variety of sensitivity coefficients. An ever present danger in system reduction is subsequent misuse of the simplified model in situations contrary to the assumptions underlying the lumping procedure; in general, model reduction needs to be performed again for each new objective.

H. Model Expansion

Although model reduction using sensitivity or other techniques represents a well established objective, a much more difficult approach to model improvement entails the expansion of an oversimplified model to a proper level of sophistication. In general, this problem is not well posed, but there is a simple quantitative indicator of model expansion that can be performed using sensitivity analysis. In particular, a common circumstance arises when the actual model calculations are performed on a simplified system drawn from a larger body of facts or information as input. For example in the case of chemical kinetics, often hundreds of possible chemical reactions could be identified as potentially important beforehand while typically only a small subset would actually be included in the first zeroth order model. In essence, one may view the results of such a calculation as involving the full extended model but with the appropriate parameters set to a null value. Although the nominal solution clearly does not contain these parameters, the gradient of the solution may still be nonzero. Therefore, the sensitivity of the additional parameters about their nominal null values can be quite easily calculated if (a) an extended "shopping list" of possible additional system components is available and (b) if the additional components do not introduce further dependent variables. Such a sensitivity to missing model components can be used to que likely new parameters for introduction into the model at their finite realistic values. Limited applications of this type have been carried out in chemical kinetics.

I. Parameter Space Mapping

Both functional and parametric gradient sensitivity analysis techniques are inherently local in nature in that the gradients are evaluated at a nominal point in parameter or input function space. Such an analysis seems often quite adequate to establish which aspects of a model are important. As commented earlier, this latter goal is often the primary motivation for applications in chemistry and physics. On the other hand, in engineering and certain scientific applications optimization is the ultimate objective.

Inherently, an optimization entails a search through parameter space and gradient techniques have an evident limitation. No satisfactory solution is available for circumventing this difficulty, but some interesting new tools involving Lie group techniques seem especially attractive. This approach considers the calculation of a Lie generator (first order differential operator) for prescribing transformations throughout the parameter space. At this stage only preliminary mathematical analysis and elementary applications have been considered.

CONCLUDING COMMENTS

Sensitivity analysis clearly provides a powerful set of systematic tools to analyze models for their physical content and mathematical behavior. Although extensive applications to scientific problems are relatively recent, there is much to be gained by an exchange of techniques and ideas between the engineering and scientific disciplines. Finally, one caveat always worth keeping in mind is that the conclusions of a sensitivity analysis will always be predicated on the significance or validity of the underlying model. However, such caution should never be used as an argument to not perform a sensitivity analysis, since any model calculations without a sensitivity analysis will be far less worthwhile.

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